General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

3. Quarterly Progress Report

Subject: NASW 3081

Title: "Bismaleimide Resins for Flame Resistant Honeycomb Sandwich Panels"

Technical Monitor: Mr. D.A. Kourtides (Code 223 - 6)
NASA/Ames Research Centre
Chemical Research Projects Office
Moffett Field, CA 94035

March 30th, 1978

Title: "Bismaleimide Resins for Flame Resistant Honeycomb Sandwich Panels"

INTRODUCTION:

Processing of advanced non-flammable Bismaleimide-type Nomex Honeycomb Core sandwich panels is a still existing problem. New resins and fabrication processes to obtain high flatwise tensile properties are still requested. Under this contract (NASW - 3081) a family of new resins (Code M751 and Code M756) will be evaluated for the

- fabrication of improved glass fabric face sheets by use of resin M751.
- fabrication of improved Nomex-Polybismaleimide Honeycomb core by use of resin M756.

In addition a new hot melt (non solvent) Bismaleimide-type resin will be formulated to overcome the state of the art solvent-resin technology, which is still used for the fabrication of glass fabric prepregs.

This third quarterly progress report summarises the work performed during the period January, February and March 1978.

RESIN M751:

The chemistry of this resin was provided in the first quarterly progress report and a 10 kg batch of the material (batch no. T_4) was delivered to NASA-Ames Research Centre in December 1977. To fabricate 100 kg of glass fabric prepregs a new 60 kg batch (batch no. T_6) of the M751 resin was produced on a pilot plant scale. The resin properties of this batch (T_6) are provided in Table 1 and compared with those of former batches.

Table 1: M751 Resin Properties

Property	BATCH NO. LB	T_2	T_4	T_8	T_9
T_{os} (DSC, 10°C/MIN) [°C]	124	132	135	127,5	---
T_{max} (DSC, 10°C/MIN) [°C]	137	146	149,5	142	---
Density [1] g/cm³	---	1,32	1,31	1,29	---
T_{D10} (TGA, 10°C/MIN)	---	---	---	400	---
Solution viscosity - ageing [2]	NMP 50%	NMP 50%	NMP 50%	NMP 50%	NMP 47%
η in [cSt]	470 - 560	411	295	422	353
η 5 d [cSt]	580 - 705	510	380	680	525
η 10 d [cSt]	735 - 890	645	465	960	710
η 20 d [cSt]	1220 - 1500	740	680	1500	1120

1 Density of cured Resin

2 Ageing temperature 20°C

T_{os} = onset temperature of DSC - peak

T_{max} = temperature of DSC - peak maximum

Density of cured Resin

T_{D10} = Decomposition temperature from TGA - curve. After 10% weight loss, heating rate 10°C /Minute

Melting behaviour of the resin:

As a quality control the melting behaviour of the resin is tested by using the Du Pont Thermal Analyser 900 in combination with the DSC-unit. Figure 1 presents the DSC-trace of the neat uncured resin. As compared with the 10 kg delivery of December (batch T_4), the onset temperature (T_{os}) and the peak temperature (T max) are lower, but higher than those of the typical laboratory batch (LB). The scale up of the laboratory procedure for the resin fabrication can lead to a batch to batch variation of the melting behaviour. But these variations obtained for all batches tested (table 1) are not significant for the use as a laminating resin.

Density of the neat cured resin:

The density of the cured resin is used to test the polymerisation behaviour and the flow properties of each resin batch. The procedure to prepare a dense void free transparent resin disc (thickness 1 - 2 mm) is given below.

Tooling: heated platen press

1) Preheat mould parts or platen press to 180°C.
2) Preform the resin powder at room temperature at 300 - 400 kg/cm^2.
3) Add the preformed M751-pill to the heated mould or between the platen press.
4) Heat the preformed M751-pill for 10 minutes at 180°C.
5) Apply pressure (20 - 50 kg/cm^2).
   (The pressure should be applied slowly to prevent squeeze out of resin).
6) Hold for 5 minutes at 180°C.
7) Heat to 220°C and cure for one hour.
8) Post cure for 15 hours at 210 - 220°C.

If no mould to preform M751-powder is available the M751 powder can be moulded betweeen aluminium foils alternatively. By use of this procedure a dense void free neat resin sample can be cut from the centre of the disc, which is transparent and useful for the density measurements. The ability to obtain a dense transparent moulded neat resin disc shows that good flow properties are to be considered. These tests also showed that the resin is useful for transfer moulding. The densities obtained for the different batches are between 1,29 - 1,32 g/cm^3 (table 1).

Viscosity-time profile:

The usual prepregging technology is based on low viscosity impregnation varnishes to apply resin onto the reinforcement. Drying of the prepreg is necessary to strip off solvent. Because of the chemical reactivity many Bismaleimide-type Resins tend to advance in solution leading to increased solution viscosities. The advancement depends on the temperature and the solvent system used. For the resin system M751 the preferred solvent is NMP (N-methyl-pyrrolidon), but DMAC (Dimethylacetamide) or DMF (Dimethylformamide) can be used as well. The figure 2 provides the viscosity-time profiles for the M751 resin batches T_4 and T_8. Batch T_8 was measured in all the three solvents mentioned above. For 50% by weight solutions DMF gave the lowest viscosity and NMP the highest. All the viscosity-time profiles obtained are typical for the resin M751.

In Figure 2 there is provided the viscosity profile of a 47% by weight solution of resin T_8 dissolved in NMP, which is coded T_9. This is the solution which was prepared from batch T_8 resin and delivered to the prepreg-company to fabricate the 100 kg glass fabric prepregs. This solution was aged at two different temperatures.

- at room temperature to compare with other batches.
- at 4°C, which is the cool-room temperature of the prepreg company.

As was to be expected at low temperature (4°C) only a slow viscosity increase upon ageing is obtained.

At this point it is necessary to consider a glass fabric prepreg as a resin solution because of the rest solvent content of 2 - 10% by weight. Therefore it is clear that advancing of the resin will occur upon ageing on the prepreg even at room temperature, and simultaneously will lead to a loss of flow properties. From this point of view resins that show viscosity stable impregnation solutions will produce prepregs with improved storage life.

Prepreg fabrication:

According to contract NASW-3081 two types of glass fabric prepregs from resin M751 had to be fabricated and delivered to NASA-Ames Research Centre.

A) 50 kg from glass fabric US-style 181, Resin content around 30 - 35% by weight, rest solvent content: as low as possible to produce (around 3 - 5 % by weight).
B) 50 kg from glass fabric US-style 120, Resin content around 35% by weight, rest solvent around 15% by weight to obtain drape and tack.

For this purpose a 47% by weight solution (120 kg) of the resin in NMP was prepared by Technochemie and delivered to the prepreg company (Firma August Krempel, 7143 Vaihingen/Enz 2 - Enzvaihingen, Postfach 240, Bundesrepublik Deutschland). Both prepreg types were produced by using standard industrial prepregging equipment on March 13th, 1978.

The following prepreg properties were obtained:

Prepreg GGHH 3006 (this is the glass fabric style 181 material)
Resin: M751

Prepreg Area weight		467 - 478 g/m^2
Glass fabric weight		290 g/m^2

Resin content (1)	37,9 - 39,3 % by weight
Solvent content (2) (loss on drying 10 minutes, 160°C)	2,4 - 2,7 % by weight
Solvent content (3) (loss on drying 2 hours, 210°C)	5,1 - 5,3 % by weight
Flow (4)	16 - 20 % by weight

Prepreg GGHH 1007 (this is the glass fabric style 120 material)

Prepreg Area weight	163,5 g/m^2
Glass fabric weight	103,3 g/m^2
Resin content (1)	36,8 % by weight
Solvent content (2)	17,7 % by weight
Flow (5)	

(1) Resin content = Dry resin and Rest solvent
(2) As determined by the prepregger
(3) As determined by Technochemie
(4) 6 layers of prepreg, pressure 20 kg/cm^2, temperature 170°C, size 7,5 x 7,5 cm.
(5) 10 layers of prepreg, pressure 20 kg/cm^2, temperature 170°C, size 7,5 x 7,5 cm.

At the prepregger, the solvent content is usually determined by drying the prepreg for 10 minutes at 160°C. But it is well known that higher temperatures are necessary to strip off all the solvent retained. The loss on drying at our laboratory is determined by drying the prepregs at 210°C for 2 hours in a circulating air oven.

The prepreg materials specified above have been delivered to NASA-Ames Research Centre on March 23rd, 1978.

Drying curves for M751/181 - Prepregs

The typical laboratory procedure to prepare prepregs consists of passing dried glass cloth through the 40 - 50% by weight solution of the M751 - Resin and removal of excess resin by passing the impregnate between a pair of steel rollers. To adjust a specific rest solvent content the prepregs are dried

in a circulating air oven. The rest solvent content is a function of the drying temperature and the drying time used. Figures 3 and 4 provide the drying curves for M751/181 - prepregs, prepared from NMP and DMAC solutions, at various drying temperatures.

As was to be expected, high temperatures are necessary to adjust low rest solvent content in the prepregs prepared from NMP. For moulding thick laminates, a very low solvent content is necessary to obtain good high temperature mechanical properties.

If we compare the prepreg quality for the 181-style material of the prepregger (5% rest solvent content) with the experimentally determined drying curves , we can see that drying for 15 minutes at 140°C in a circulating air oven will provide the same rest solvent content as obtained by the prepreg manufacturer.

Curing cycle for M751/181 - laminates:

The following curing cycle was used to prepare a 10 layer (10 x 10 cm) laminate from prepregs fabricated by the prepregger.

Tooling: heated platen press

1) Preheat platen press to 170°C.
2) Insert a stack of 10 layers of M751/181 prepregs between aluminium foils into the press.
3) Kiss contact for one minute.
4) Apply pressure of 20 to 40 kg/cm^2.
5) Hold temperature and pressure for two hours.
6) Cool to room temperature.
7) Post cure for 15 hours at 210°C.

The following room temperature mechanical properties of the laminate are obtained. The flash (squeeze out) was 5% by weight.

Laminate properties: (M751/181 - 10 layer laminate)

Laminate thickness	2,35	mm
Resin content	32 %	by weight
Density	1,88	g/cm^3
Flexural strength (1)	556	$N. mm^{-2}$
Flexural modulus	23,4	$KN. mm^{-2}$
ILSS (2)	53	$N. mm^{-2}$

(1) Span to depth ratio 16:1 (ASTM D 790 - 66)
(2) Span to depth ratio 5:1

Thermal gravimetric stability of M751 - Resin

The TGA-curve for the neat M751 - Resin (batch T_g) is provided in figure 5. The sample investigated was moulded as described for the density sample preparation. For comparison the TGA-curve of the resin flash obtained from the moulded laminate is provided too (figure 5). It can be seen that the TGA break of the material that has been in contact with the solvent N-Methylpyrrolidon occurs at lower temperatures. Also the char yield is lower. This example again shows that processing of high temperature non-flammable resins by using high boiling solvents has to be done very carefully to prevent high residual solvent in the laminate. For thin face sheets this phenomenon is not so critical because post drying of the cured thin face sheet can provide a low rest solvent content. Therefore the following curing procedure for the fabrication of M751/181 - prepregs is recommended:

1) Cure face sheet for 2 hours at 170°C at a pressure of 7 kg/cm² between aluminium plates (mould release).
2) Post cure for 15 hours at 210°C in a circulating air oven.

This cycle is used by Technochemie to cure M751/181 prepreg face sheets.

Resin M756

Basic improvements for the production of sandwich construction comprising strong thin facings (Bismaleimide-type) and a thick lightweight honeycomb core need to be developed. The approach in mind is to bond B-stage face sheets (M751/181 prepregs) to a B-stage bismaleimide-resin impregnated honeycomb core in one step. Bismaleimide-type B-stage Nomex honeycombs are so far not available. To impregnate prime cured Nomex honeycombs the resin M756 was selected because it is soluble in low boiling solvents like acetone and tetrahydrofurane. Resin chemistry was provided in the last progress report (December 1977), also a 1 kg sample of this resin was delivered to NASA Ames. This resin of the first delivery is now coded Resin M756-1. In contrast to the former, this resin gave no stable solutions in acetone or THF. We therefore again reinvestigated the molar ratios between m-maleimido-benzoic acid chloride and diaminodiphenylsulfone The change to a molar ratio of 1:0,7 gave an acetone and THF soluble material. 0,5 kg of this new resin was delivered to NASA-Ames Research Centre at the end of March 1978. Viscosity-time profiles are under investigation. The following starting viscosities are obtained:

Sample: Resin M756-2 (Batch no. M1234/3)

- 40% by weight in acetone 2,64 cStokes
- 50% by weight in THF 24,73 cStokes

The viscosity-time profiles for this modification are still under investigation.

Honeycomb sandwich development:

The development of Bismaleimide resin type sandwich panels in this programme consists of the following steps.

1) Preparation of face sheets from M751/181 - prepregs
2) Development of a laboratory procedure for B-staged Nomex M756 honeycomb core

3) Evaluation of the flatwise tensile properties of composite panels fabricated from B-stage M751/181 face sheets and Nomex M756 honeycomb core by a one-step curing process.

add. 1) The face sheet development is finished and the preparation of cured samples is performed as given above. For the one-step bonding the prepregs as delivered by the prepregger will be used.

add. 2) Initially it was tried to prepare by simply immersing the prime cured Nomex core in a 50% by weight solution of M756-1 in acetone, followed by drying at room temperature to 100°C in a circulating air oven. This procedure led to non-uniform impregnation and to a blistering off of the dry brittle resin in the uncured dried state, because of the low film forming properties of the M756-acetone varnish. Several other solvent combinations were therefore tested and it was found that uniform impregnation could be obtained by using a high boiling solvent like DMAC in combination with tetrahydrofurane (THF). Solvent combinations of 5 - 10% DMAC and 95 - 90% THF are preferably used. Resin concentrations of 25 - 30% provide a resin pick-up of the honeycomb of 30 - 32% by weight. Stepwise drying in a circulating air oven produces dry B-stage honeycomb material.

As a result of this preliminary investigation, it seems to be rational to consider not only M756-Resin for honeycomb impregnation, since a small amount of high boiling solvent is necessary to produce stable, uniformly impregnated B-stage honeycomb core.

As the next step, the detailed procedure for the impregnation will be worked out and the compressive strength of cured Nomex M756 honeycombs will be evaluated.

add. 3) Base-line panels which will be used for comparison have been fabricated (flatwise tensile properties) by use of an epoxy film adhesive, Nomex phenolic resin honeycomb core and M751/181 facings.

Hot melt resin:

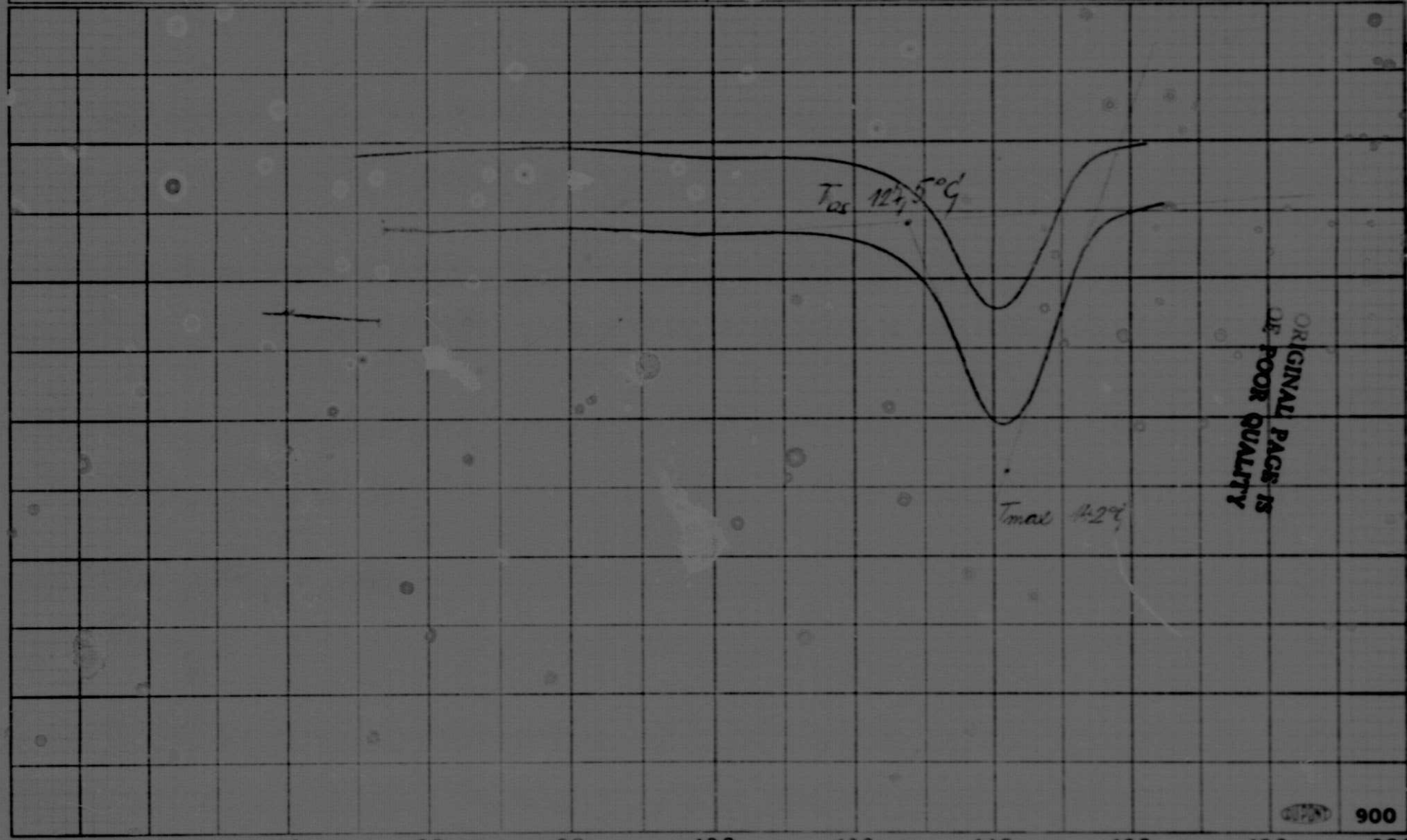
This resin (1 kg) will be delivered at the end of May.

Dr.Stz/sy

31st March, 1978

DUPONT INSTRUMENTS

SAMPLE: M 71 / 72	SIZE	ATM.	RUN NO. 337
	REF. Al$_2$O$_3$ Calcinée	T / ΔT	DATE 3 2 1972
	PROGRAM MODE Heat	SCALE SETTING 20 / 0,5	OPERATOR Magnabosco
ORIGIN:	RATE 10 °C/min. START °C		



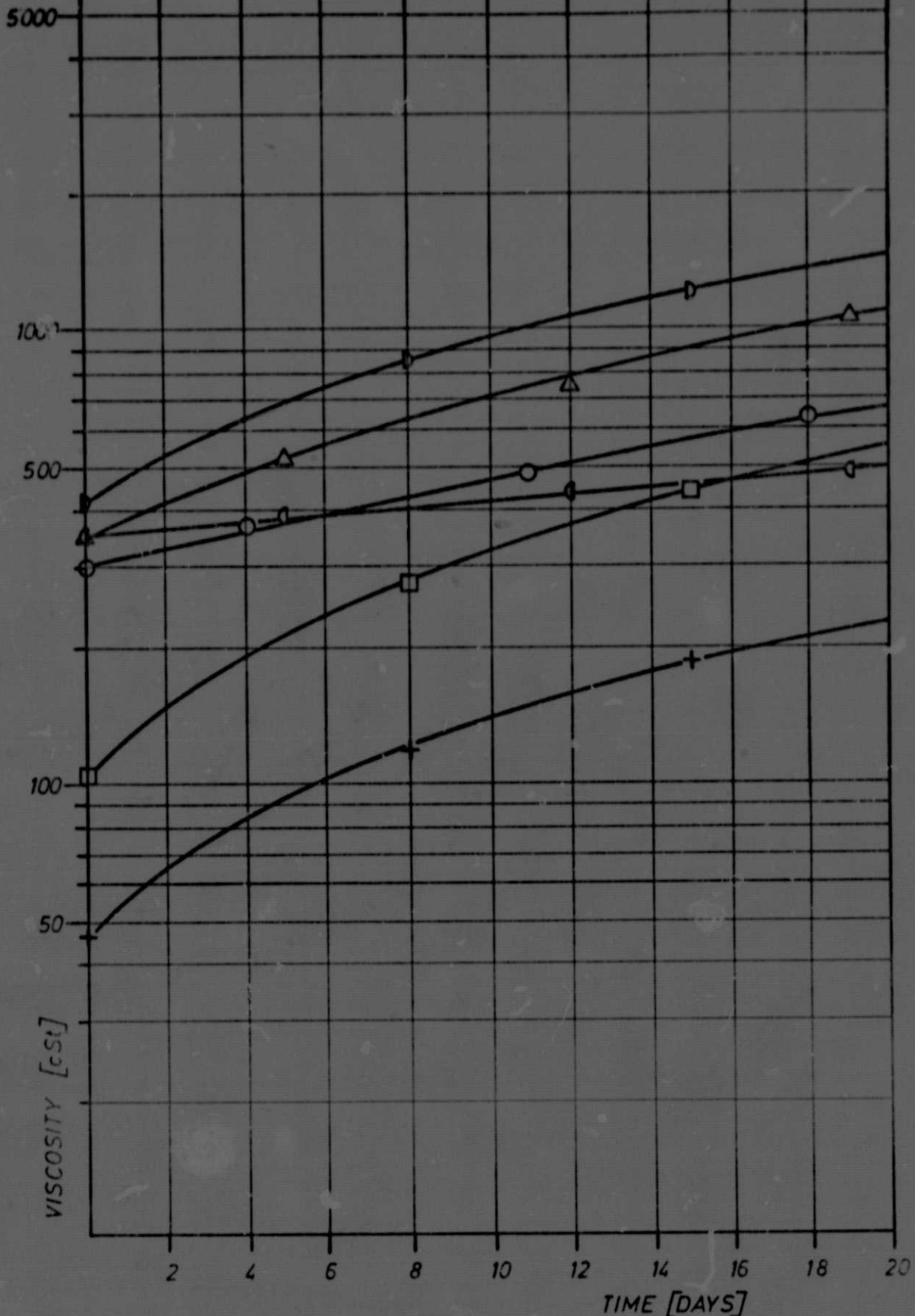


Figure 2: Viscosity-Time profiles of M 751-resin solutions

○ T4 in NMP 50%ig
□ T8 in DMAc 50%ig
+ T8 in DMF 50%ig
◗ T8 in NMP 50%ig
△ T9 in NMP 47%ig, aging at 20°C
◖ T9 in NMP 47%ig, aging at 4°C

Figure 3: DRYING CURVES for M751/181-PREPREGS

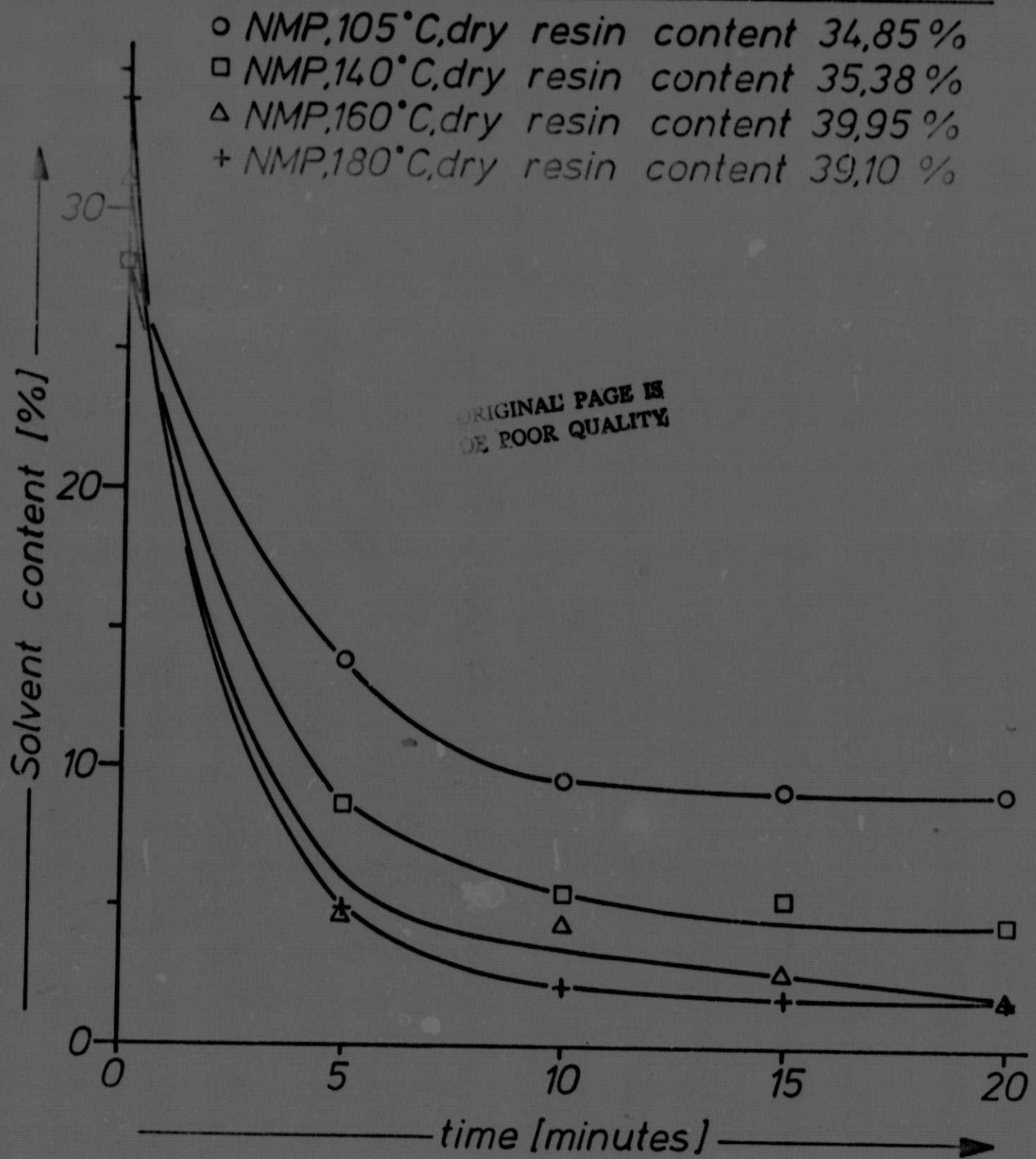
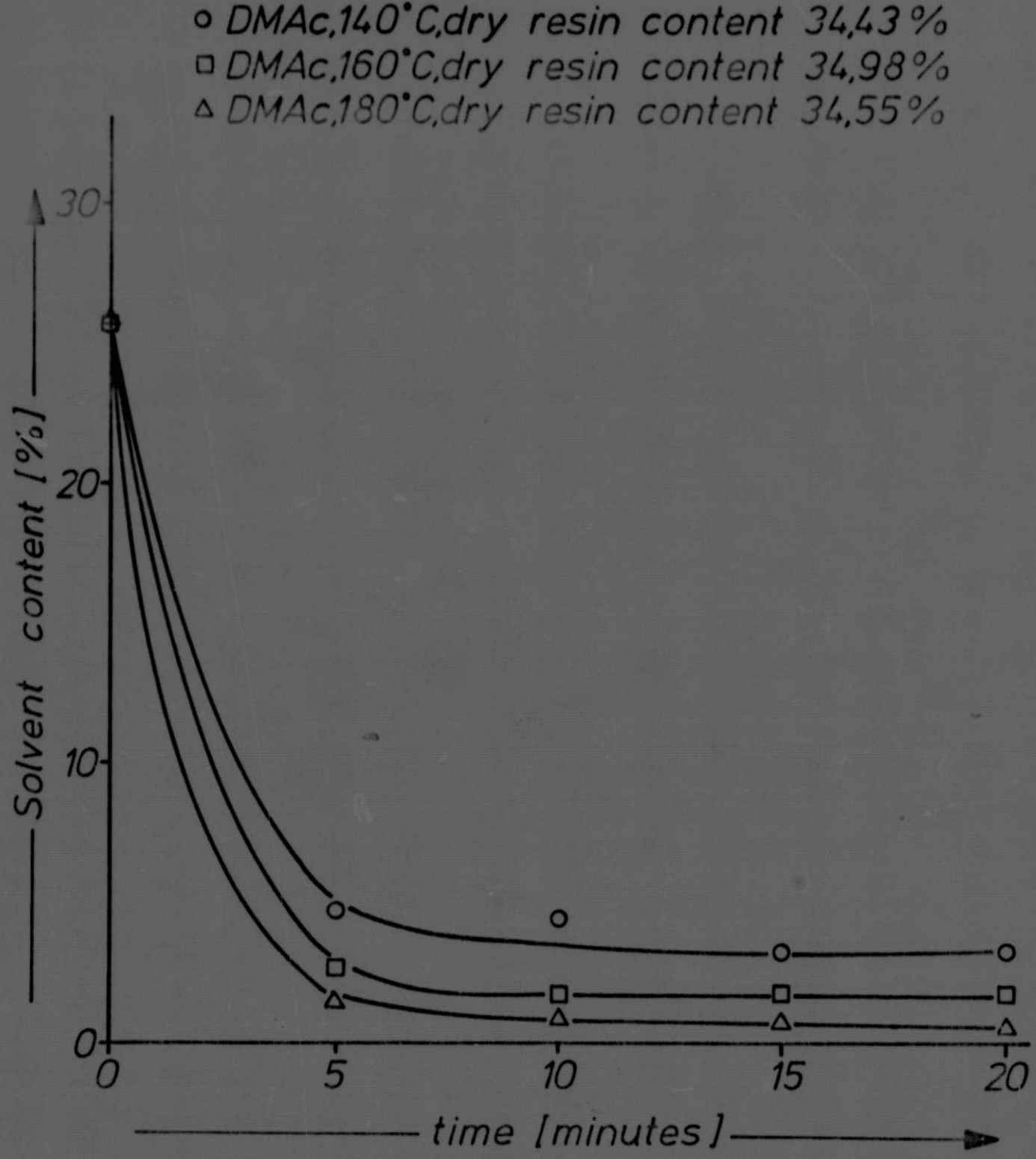


Figure 4: DRYING CURVES for M751/181 PREPREGS



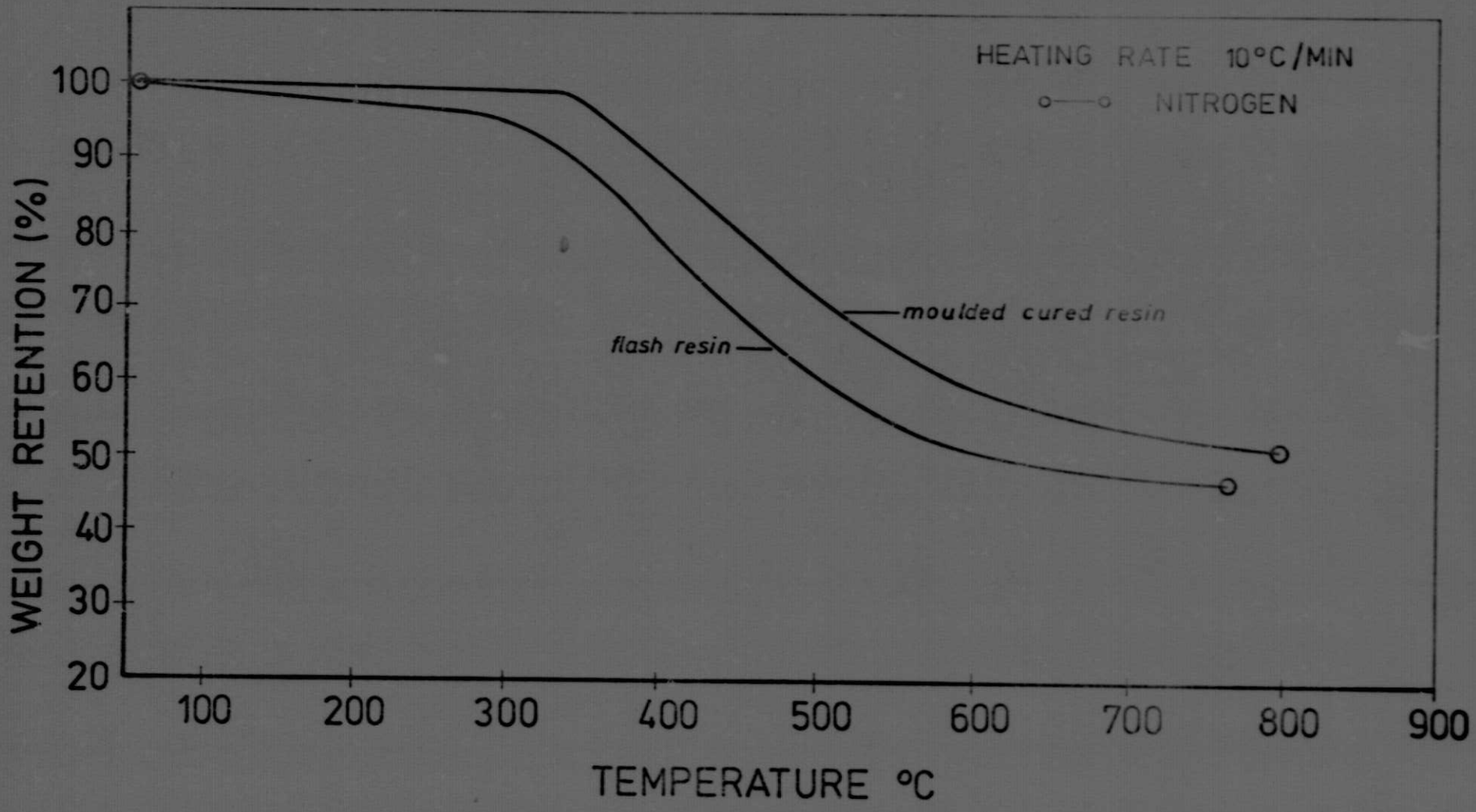


Figure 5: TGA-THERMOGRAMMS OF BISMALEIMIDE RESIN M751